PB84-101773

Residues of PCB (Polychlorinated Biphenyls) in a 'Cladophora' Community Along the Lake Huron Shoreline

Michigan Univ., Ann Arbor

Prepared for

Environmental Research Lab.-Duluth, MN

1982

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
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1. REPORT NO.	2.	3
EPA-600/J-82-387		PB84-101773

4. TITLE AND SUBTITLE	5. REPORT DATE
Residues of PCB in a Cladophora Community Along the Lake Huron Shoreline (Journal Version)	1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
M.L. Anderson, C.P. Rice, and C.C. Carl	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Great Lakes Research Division The University of Michigan Ann Arbor, Michigan 48109	11. CONTRACT/GRANT NO. 806600
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency Environmental Research Laboratory-Duluth 6201 Congdon Boulevard Duluth, Minnesota 55804	14. SPONSORING AGENCY CODE EPA/600/03

15. SUPPLEMENTARY NOTES
J. Great Lakes Res. 8(1): 196-200 (1982)

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
	UNCLASSIFIED	7
RELEASE TO PUBLIC	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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EPA-600/J-82-387
JOURNAL ARTICLE

J. Great Lakes Res. 8(1):196–200
Internat. Assoc. Great Lakes Res., 1982

RESIDUES OF PCB IN A *CLADOPHORA* COMMUNITY ALONG THE LAKE HURON SHORELINE

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ABSTRACT. *PCB residues were measured in samples of* Cladophora, Ulothrix, *net plankton, water, and fish collected in the Harbor Beach area of Lake Huron. The average concentrations of total PCB in each of the sample groups were as follows: water - 0.154 ng/g;* Cladophora *- 92 ng/g;* Ulothrix *- 126 ng/g; net plankton - 1,651 ng/g; and fish - 40 to 4,400 ng/g. The PCB patterns in the samples were found to match a mixture of Aroclor 1242 and 1254. Aroclor 1242 represented about 60% of the mixture in all the samples except the fish, where Aroclor 1254 represented about 75% of the total PCB measured. The accumulation factors observed in the progression from* Cladophora *to net plankton to fish were 1:15:30; these were similar to the concentration factors (1:14:44) developed on these ecosystem compartments in Lake Ontario during the 1972 IFYGL program.*

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of organic industrial compounds formed by the chlorination of biphenyl. They have become widespread contaminants of all portions of the environment and are a cause for concern due to their linkage to a number of physiological abnormalities in animals and their bioaccumulation in aquatic food chains (National Research Council 1979).

In the Great Lakes ecosystem the problem of PCBs is especially acute. The concern arises from the occurrence of high residues of PCB occurring in fish consumed by humans. Reduced to its simplest form, the problem developed because of the property of PCBs to bioaccumulate. A method of portraying this biomagnification is to compare the concentration of a chemical in different segments of a simplified food chain (Thomann 1981). In this present study, components of the nearshore zone at Harbor Beach, Michigan, were investigated to determine the levels of PCB accumulation. Of particular concern was the accumulation of PCBs by *Cladophora*, an alga whose growth has become a problem in numerous nearshore zones around the Great Lakes. It was also a purpose of this study to determine the concentration factors of each of the ecosystem components relative to the water.

METHODS

Chemicals and Glassware

Pesticide grade solvents were used for all of the analyses. Petroleum ether, hexane, and methylene chloride were obtained from Burdick and Jackson, Muskegon, Michigan. Activity grade I Woelm neutral alumina was obtained from ICN Pharmaceuticals, Cleveland, Ohio. Aroclors 1242 and 1254 were obtained from the U.S. Environmental Protection Agency, Environmental Toxicology Division, Research Triangle Park, North Carolina. All other chemicals were reagent grade. The glassware was washed in hot soapy water, rinsed with tap water, rinsed with distilled water, and allowed to air dry. The glassware was triple rinsed with petroleum ether just prior to use. The Mason jars used for collection of the *Cladophora* and fish were sealed with aluminum foil-lined lids.

Sample Handling, Extraction, and Quantitation

Cladophora, lake water, and fish were collected during July 1979 at the stations indicated in Figure 1. The *Cladophora* was collected from rocks in the

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nearshore zone, placed in clean Mason jars, and frozen. Fish were collected by seining at night in the nearshore region. The fish were separated according to species and stored frozen prior to analysis. Net plankton were collected using a No. 10 Nitex net (net aperature = 153 microns).

Six-liter water samples were collected in clean, one-gallon pesticide grade solvent bottles and refrigerated at 4°C. The water samples were filtered through Gelman A glass fiber filters using a Millipore vacuum filtration system. The filters were heated to 400°C for 4 hours and sealed in aluminum foil packets in order to free them of contamination prior to use. The filter and suspended solids removed from the samples were stored frozen prior to analysis. Two hundred mL of methylene chloride were added to the 3 L of water in each jug and extracted for 4 hours on a jar mill. Each water sample was extracted a second time with hexane using a separatory funnel. The hexane and methylene chloride extracts were combined, dried by passing them through a sodium sulfate column, and then concentrated to less than 2 mL in a Kuderna-Danish (K-D) evaporative concentrator on a steam bath. The *Cladophora* and filters from the water samples were freeze-dried and soxhlet extracted (100 cycles) with petroleum ether. The petroleum ether extracts were concentrated to less than 2 mL in a K-D system.

Six fish of each species were homogenized and a subsample taken for the PCB analysis. The subsample was mixed with a portion of Na_2SO_4 equal to two times its weight. This dried fish sample was then soxhlet extracted (100 cycles) with petroleum ether. The extract was concentrated in a K-D apparatus to less than 2 mL. Sequential extractions of fish and *Cladophora* indicated that more than 99% of the recovered PCBs were contained in the petroleum ether of the first 100 cycle extraction period.

An alumina procedure (Holden and Marsden 1969) was used for extract cleanup. This was prepared by placing 4 g of alumina (converted to activity III by addition of 6% water) in a glass column (9 mm × 30 mm) and topping it with one-half inch of anhydrous Na_2SO_4. The PCB-containing eluate from the alumina cleanup step was collected in a K-D flask and concentrated prior to fractionation on a silicic acid column. This procedure provided separation of the extracts into PCB and organochlorine pesticide fractions (Bidleman *et al.* 1978). Sulfur was found to be a contaminant of some of the extracts. This was removed from these extracts just prior to GC injection by mixing them with elemental mercury (Goerlitz and Law 1974).

Quantitation and identification of the materials in the samples was performed using a Varian 3700 gas chromatograph equipped with a Ni^{63} electron capture detector. The operating conditions for the GC were: injection temperature 220°C, column

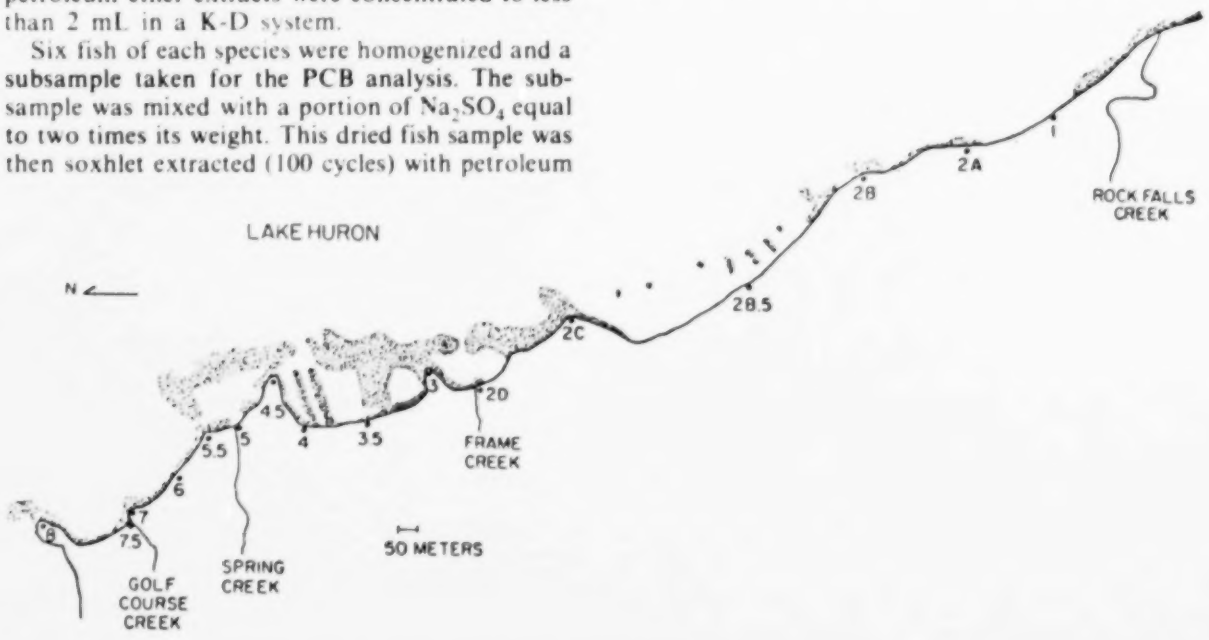

FIG. 1. Location of sampling sites along the Lake Huron shoreline near Harbor Beach, Michigan. Stippled areas on the map indicate regions of high* Cladophora *growth for this period.

temperature 199°C, detector temperature 350°C, gas flow (nitrogren) 30 mL/min. The column was a 2-m-long, 2-mm ID glass column packed with 4% OV101/6% OV210 coated on 80/100 mesh chromsorb W-HP. The quantities of Aroclor 1242 and 1254 contained in the samples were determined by the method of the Association of Official Analytical Chemists (Food and Drug Administration 1977).

RESULTS AND DISCUSSION

Detectable quantities of PCB were found in all of the water samples that were collected. These results are presented in Table 1. The chromatograms for the residues were composed of a mixture of Aroclors, with most of the peaks accounted for with standard mixtures of Aroclor 1242 and Aroclor 1254. The concentration of Aroclor 1242 in the water samples averaged 91 ng/L while Aroclor 1254 was 63 ng/L. The total PCB concentration of 154 ng/L included both dissolved (52%) and particulate (48%) phases. The total PCB concentration is considerably higher than the 55 ng/L reported by Haile *et al.* (1975) for the waters of Lake Ontario or the limit of detection of 100 ng/L reported by Glooschenko, Strachan, and Sampson (1976) for Lake Huron. The proportion of Aroclor 1242 to Aroclor 1254 which was in the dissolved phase is also much lower than what would be expected from solubility studies (i.e. Aroclor 1242 is more soluble than Aroclor 1254) reported by Tulp and Hutzinger (1978). Two days prior to the sample collection in this study a major storm event passed through the area causing a significant resuspension of sediments in the nearshore zone. This resulted in extremely high turbidity (Secchi disc reading less than 1 m). The presence of these high suspended solids could explain the relatively high concentrations of PCBs found in the water. Also this recent storm event may not have provided adequate time for an equilibrium condition to establish itself in order to make the solubility differences of Aroclor 1242 and Aroclor 1254 discernible by our results.

The *Cladophora*, *Ulothrix*, and net plankton results are contained in Table 2. The *Cladophora* averaged 92 ng/g dry weight of total PCBs. Approximately 58% of this total was in the Aroclor 1242 fraction. This is very similar to the proportion of Aroclor 1242 contained in the water. The PCB level of *Cladophora* is considerably less than that reported for Lake Ontario by Haile *et al.* (1975) who found 515 ng/g dry weight. This lower level may reflect a lower total burden of PCBs in Lake Huron than in Lake Ontario (Environment Canada 1976). Analysis of the samples for the DDT group pesticides, chlordane, and dieldrin was also done but only DDE was found in the *Cladophora*. For most of the samples, DDE was near the limit of detection of 1 ng/g dry wt. *Ulothrix* was only found at two sample locations and its PCB concentration did not differ significantly from that found in *Cladophora*. The net plankton averaged 1,651 ng/g dry weight of total PCBs, with Aroclor 1242 comprising 62% of the total. This percentage of Aroclor 1242 is similar to that observed in the *Cladophora* and the water.

The PCB concentration of the fish ranged from 40 ng/g to 4,400 ng/g recorded as wet weight of

TABLE 1. PCB concentrations in Lake Huron water samples collected south of Harbor Beach, Michigan.

	Aroclor 1242		Aroclor 1254		Total PCB	
Station Number	Concentration (ng/L)	Percent Dissolved	Concentration (ng/L)	Percent Dissolved	Concentration (ng/L)	Percent Aroclor 1242
1	521	84	65	63	586	89
2A	104	35	53	45	157	66
2B	84	29	63	73	147	57
2C	150	70	107	89	257	58
3	71	70	129	83	200	36
4	109	23	34	27	143	76
4.5	105	42	139	91	244	43
5.5	31	58	14	18	45	69
6	75	61	36	10	111	67
8	28	51	6	55	34	82
Off Shore	155	64	22	45	177	88

TABLE 2. PCB concentrations in Lake Huron biota collected south of Harbor Beach, Michigan.

Station Number	Aroclor 1242 (ng/g dry wt.)	Aroclor 1254 (ng/g dry wt.)	Total PCB Concentration (ng/g dry wt.)	Total PCB Percent 1242	ppDDE (ng/g dry wt.)
CLADOPHORA					
2A	73	24	97	75.2	<1
2C	26	17	43	60.5	5.1
3	31	10	41	75.6	8.7
4	42	40	82	51.2	10.3
4.5	120	71	191	62.8	9.3
5.5	16	17	33	48.5	2.7
6	79	85	164	48.2	<1
8	40	41	81	49.4	6.1
Average	53	38	92	58.9	5.5
ULOTHRIX					
2A	46	47	93	49.5	<1
2B	60	12	72	83.3	1.2
Composite Sample	105	108	213	49.3	<1
Average	70	56	126	60.7	
PLANKTON					
2A	920	730	1,650	45.8	<5
4	1,410	260	1,670	84.4	<5
Off Shore	310	760	1,380	40.8	<5
Off Shore	1,500	405	1,705	78.7	<5
Average	1,035	539	1,651	62.7	

whole fish. The results are presented in Table 3. These values are similiar to results for comparable species obtained by the International Joint Commission (1977) and Michigan Water Resources Commission (1975). The percentage of Aroclor 1242 is much less than that of Aroclor 1254. This selective fractionation of heavier chlorobiphenyls is in agreement with similar findings reported by Weininger (1978).

In a study conducted in Lake Ontario during the International Field Year for Great lakes (IFYGL) in 1972 (Haile *et al.* 1975), various compartments of the ecosystem were sampled and analyzed for organochlorine compounds including PCBs. The average concentration of PCB in the Lake Ontario fish (alewives, slimey sculpin, and smelt) was 3,440 ng/g; for water, the concentration of PCB was 2–6 ng/L (revised from Haile's original value of 55 ng/L—Waller and Lee 1979); for sediment the average value reported was 120 ng/g; for benthos it was 471 ng/g; for *Cladophora* it was 515 ng/g; and for net plankton it was 7,200 ng/g. Haile *et al.* (1975) compared the relative concentrations of the chlorinated hydrocarbons in these various compartments and indicated concentration factors of 10,000 to 300,000 for benthic organisms and fish. These concentration differences indicate the large accumulation factors that are operative when these compounds interact with the lake shore environment. In order to apply a similar treatment to our data, the uptake of PCBs by one organism group was compared to the uptake by the other groups. To do this, all of the organism levels have to be expressed on the same basis. If an 85% moisture content is assumed for *Cladophora*, *Ulothrix*, and net plankton, the PCB levels can be compared with those of the fish. The water concentration was used as a basis for relative comparison of the three organism groups, which permitted a ratio of water to *Cladophora* to net plankton to fish of 1:90:1,500:3,000 to be obtained. This ratio of PCB concentration by organism level is similar to that presented in the study by Haile *et al.* (1975) for Lake Ontario. The PCB concentrations, however, were higher in the Lake Ontario study. For example, the relative differences of water to *Cladophora* to net plankton to fish in their study was 1:19,000:270,000:850,000. The absolute differences in the two data sets for Lake Huron and Lake Ontario are obviously biased by the differences in their water concentrations. However, even assuming a more reasonable concentration for water for our Lake Huron data such as 4-10 ppt, the concentration factor from water to *Cladophora*

TABLE 3. PCB concentration in Lake Huron fish collected south of Harbor Beach, Michigan.

Fish Species	Aroclor 1242 (ng/g wet wt.)	Aroclor 1254 (ng/g wet wt.)	Total PCB Concentration (ng/g wet wt.)	Total PCB Percent Aroclor 1242
Alewife	110	340	450	24
Spottailed Shiner	76	538	614	12
Emerald Shiner	14	26	40	35
Carp	123	319	4,420	28

becomes 2,300 which is still approximately 10x less than the concentration factor observed by Haile *et al.* 1975. Comparing just the ratios of the three compartments (i.e. *Cladophora*, net plankton, and fish) for the two studies the following ratios can be calculated: 1:14:44 for Haile's results for PCB and 1:15:30 for the results discussed here. These concentration factors are quite similar between the two studies.

The ratio of Aroclor 1242 to Aroclor 1254 in the water and organisms analyzed at Harbor Beach was 1.5 to 1 for the water; 1.4 to 1 for *Cladophora*; 1.9 to 1 for net plankton; and only 0.1–0.5 to 1 for the fish. This difference in the ratio of Aroclor 1242 to Aroclor 1254 between groups would seem to indicate a different mechanism of uptake for the different trophic levels. The lower trophic levels (*Cladophora*, *Ulothrix*, net plankton) reflect the ratio in the water fairly closely indicating that the mechanism of uptake might be one of simple sorption. The concentration in net plankton is also considerably higher than *Cladophora*, but the higher surface area to volume ratio of net plankton may explain this. Fish, being in the upper trophic levels, appear to retain Aroclor 1254 preferentially over Aroclor 1242 indicating that the mechanism is more complex than sorption alone. The proportion of Aroclor 1242 to Aroclor 1254 found in the various organisms does not reflect the known usage or assumed release of PCBs to the environment. For the period 1957–1974 the usage of Aroclor 1242 to Aroclor 1254 was approximately 2:1, while for the period 1974 to 1977 the ratio is estimated to be as high as 10:1 (Environment Canada 1976). An explanation for this observation is not apparent from the data presented in this study.

Our data indicate that *Cladophora* may effectively moderate the passage of PCB through the nearshore food chain. The role of *Cladophora* as a source of PCBs seems more supportable than as a sink. From our data in the Harbor Beach community, there was little or no buildup of PCB by the *Cladophora* (e.g. a concentration factor from water of 90 versus 2,300 to 19,000 for Haile *et al.* 1975).

ACKNOWLEDGMENT

This work was supported by the USEPA Large Lakes Research Station under Project No. R806800. We thank Mr. Nelson Thomas for providing suggestions and encouragement for this study. Contribution Number 306 of the Great Lakes Research Division.

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